

Chapter 4

Are Ionic Liquids Enabling Technology? Startup to Scale-Up to Find Out



Julia L. Shamshina and Robin D. Rogers

Abstract Commercialization of new sustainable technology from academia to industry is based on the technology-enabling innovation, the manufacturability, the implementation cost, and the technology's competitive advantage, such as functionality improvement(s) over the routine process or existing products. Future-minded thinking outside the accepted margins and innovative execution are involved in creating new markets. The majority of this chapter is dedicated to our experiences in pursuing the transition of ionic liquids (ILs)-based technology from academia to industry for the extraction of chitin ((C₈H₁₃O₅N)_n), the second most abundant biopolymer on the planet, directly from shrimp shells. While the dissolution and extraction of chitin was demonstrated as early as 2010, the necessity of using an IL presented hurdles for scaling the technology to a commercial level. The resultant chitin polymer could be extracted while maintaining its high-molecular weight and providing materials with high strength and unique control of the final form. In 2012, a Laboratory Demonstration Pilot Unit (LDPU) was built and tested, followed by further scale-up to a mini-pilot plant in 2014–2015 with funding from the U.S. Department of Energy. Currently, this mini-pilot plant provides the groundwork for the construction of a larger plant for a scaled-up chitin extraction by Mari Signum, Mid-Atlantic. This will allow the generation of sufficient supplies of chitin and create new markets for this polymer. The high quality of the polymer and the ability to produce high-value products from it will give Mari Signum, Mid-Atlantic a competitive advantage not only to enter multiple focused profitable markets but also to create new markets. Once the polymer becomes available on a large-scale not only will the price decrease, but it will become available for the invention of additional products. When large-scale supply is available, it will provide confidence to investors due to

RDR is president of 525 Solutions, Inc. and has partial ownership of 525 Solutions, Inc. RDR has a former ownership in Mari Signum, Mid-Atlantic, LLC. RDR and JLS are named inventors on related patents and applications. JLS is a former employee of 525 Solutions, Inc. and a former CTO of Mari Signum, Mid-Atlantic, LLC.

J. L. Shamshina (✉)

Mari Signum, Mid Atlantic, LLC, 8310 Shell Road, 23237 Richmond, VA, USA
e-mail: shams002@gmail.com

R. D. Rogers

525 Solutions, Inc., P.O. Box 2206, 35403 Tuscaloosa, AL, USA

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known and manageable marketing and supply costs. The tremendous potential of chitin will soon be exploited for a number of industrial applications utilizing the full potential of this IL-based platform.

Keywords Biomass · Biopolymers · Chitin · Commercialization · Ionic liquid · Process development · Product development · Renewable polymers

4.1 Introduction

4.1.1 *More Plastic than Fish*

With an increase in plastic production volume from about 2 million metric tons per year in 1950 to over 400 million metric tons per year in 2015, the global plastics market is expected to reach \$654 billion by 2020 [1, 2]. At the same time, recent data on the lifecycle of plastics worldwide from production to utilization to recycle suggest that as much as 76% of all plastics produced to date have ended up as waste [3]. Only 9% of this waste has been re-processed, 12% has been incinerated, and 79% has accumulated worldwide. At the current plastic production rate, the amount of plastic waste accrued in the environment will practically double by 2050 compared with 2015 [2]. The Ellen MacArthur Foundation in its 2016 report [4] claimed that if plastic continues to be manufactured at current rates with irresponsible disposal, there will be more plastic than fish in our oceans by 2050 [5].

The enormous negative environmental impact of the plastics industry [6] has resulted in a major reconsideration of the role of renewables in sustainable product development. The classic definition of sustainable product development in value-added products' manufacture is the use of renewable resources, that is, resources that can be used repeatedly and are being naturally replaced. The potential of polymers sourced from nature, or *biopolymers* isolated from biomass as a by-product of agricultural, forestry, and marine ecosystems [7], are both vital components from a sustainability and economic value standpoint.

4.1.2 *Taking Full Advantage of What Nature Creates*

The definition of biopolymers has less to do with chemistry and more to do with semantics. Any chemist dealing with sustainable development in the last few years has run into the recurrence of the term “renewable”, closely connected to “biorefinery”. The well-established biorefinery model is focused on bio-based chemicals and products in which biomass is first converted into commodity building blocks and high-value chemicals for high-volume global markets. The production of lower-cost chemical building blocks is understandable, and ultimately, society must move

towards bio-based substituents to reduce our dependence on petroleum. A biorefinery, however, is based on the idea that biomass needs to be “de-functionalized” at the cost of chemicals and energy to be made into the basic building blocks found in petroleum.

Oftentimes, these basic bio-based building blocks are utilized in polymer synthesis, and the resultant chemicals are also named “biopolymers”. For instance, polylactic acid (PLA) is known as a biopolymer even though it is a polyester derived from renewably-sourced lactic acid. In this regard, the concept of using bio-based chemicals as precursors for polymer manufacturing is confusing, since often the same non-degradable plastic is produced, regardless of whether this plastic is oil-based or plant-based. The life cycle of a plastic product is more important than its origin. For example, recently, Coca-Cola advertised its new beverage container or “plant-bottle” [8] made of polyethylene terephthalate (PET), produced by condensation of bio-based monoethylene glycol with terephthalic acid. Laboratory experiments studying PET degradation predicted a life expectancy between 27 [9] and 93 [10] years, regardless of the starting material used for manufacture.

When we talk about biopolymers in the following chapter, we mean polymers isolated from naturally occurring biomass “as nature made them” [11], such as polysaccharides (e.g., cellulose, chitin, hemicellulose), proteins (e.g., spider silk), plants polyesters (e.g., lignin), and so forth, and not the ones produced from bio-based chemicals. These biopolymers are viewed not as a replacement for petroleum, but as a source of valuable chemicals and materials that cannot be obtained from petroleum. Instead of chemically modifying polymers obtained from nature and making synthetic analogs, we need to figure out how to take full advantage of what nature does so well.

4.1.3 Research and Development to Commercialization Constraints: Need of Economy of Scale

Research and development in the field of biopolymers is primarily small in scale and academic in nature. While renewable, biodegradable replacements for plastics are being actively developed, they have come nowhere close to completely replacing plastics. Plastics enjoy technological maturity and an entrenched economy of scale that have kept new technologies from competing with them.

Economic barriers include poor predictions for short-term profits, undefined demand in the marketplace because of prevailing inexpensive alternatives (synthetic polymers), and, most importantly, a lack of supply in needed volume. Plastics rose to dominance through the availability of cheap oil as a feedstock and open markets for its products, and for any replacement to be successful, those two factors must be addressed. Because biopolymers will undeniably be more expensive than synthetic analogs, much work will be required to lower the costs. Even if some biopolymers are shown to have advantageous properties when compared to conventional polymers,

in only a few high-end applications, such as biomaterials (e.g., tissue engineering, plastic surgery, and drug delivery devices), will the relatively high costs of biopolymer precursors likely not interfere with market growth. In low-end and medium-end applications, it is hard to predict whether economy-of-scale manufacturing will be able to bring down the current high production costs.

Technical barriers are the same as for all new technologies, such as product design and long development periods, even more so taking into consideration a need for ‘bench-to-scale’ prototyping. Besides, any new process also requires development (or at least adaptation) of production equipment.

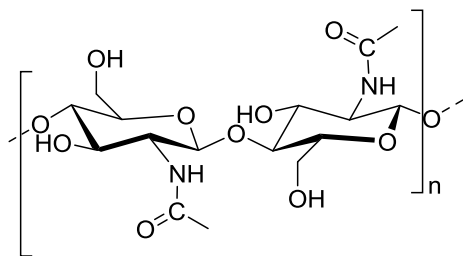
Finally, the enormous growth in the plastics economy during the twenty-first century reflects a large investment in the oil-based industry. While renewable resources are perfectly suited to provide the same rich variety of polymers and composites as that currently available from oil, there has not been the same extent of investments for renewables that have gone into plastics manufacturing. On the other hand, transition from non-biodegradable plastic materials to biodegradable biopolymeric products from renewable sources will be highly advantageous to society for development of new materials, new products, new unforeseen markets, and improvement in the environment.

4.2 Brief Foreword to Chitin and Current Isolation Technology

4.2.1 Chitin Polymer

Chitin, a linear carbohydrate made of *N*-acetyl-D-glucosamine units as shown in Fig. 4.1, is the second most abundant biopolymer on earth (after cellulose) [12] and a primary component of crustacean shells (e.g., crabs, lobsters, and shrimps), where it exists in a protein-mineral matrix. Chitin is a known wound-healing accelerator [13], has anti-inflammatory properties [14], is protein-regulating [15] and has cell-proliferating [16] properties, and demonstrates outstanding biocompatibility [17]. It is also biodegradable (12-weeks post-surgery degradation in the human body [18]), non-allergenic, and non-toxic. The polymer demonstrates high mechanical strength

Fig. 4.1 Structure of chitin



and provides the advantage of easy surface modifications [19]. Multiple reviews on chitin and its properties are available elsewhere [20–25].

4.2.2 Chitin Market

The global chitin market was worth \$803 million in 2016, increased to \$893 million in 2017, and is predicted to triple to \$2,941 million by 2027 according to Global Industry Analysis [26]. The global chitin market is projected to have a compound annual growth rate (CAGR) of 12.7% throughout the period of 2017–2027. New biomedical products are the main drivers of this market. Overall, the healthcare segment, estimated at \$309 million in 2017, is projected to grow at a CAGR of 14.2% throughout 2017–2027 and is anticipated to reach \$1 billion by the end of 2027. For instance, chitin-based materials have been proposed for artificial organs [27], space-filling implants [28], drug delivery systems [29, 30], tissue engineering materials [31], wound dressings [32], treatment of burns [33], artificial skin, and plastic skin surgery [34].

Even though there is a high demand for chitin and its derivatives, currently there is no North American producer of chitin. In 2008, there were five companies that dealt with chitin derivatives (namely, chitosan and glucosamine) including Biothera Inc., CarboMer, Inc., HaloSource, Inc., V-Labs, Inc., and United Chitotechnologies [35]. Even though some of these companies claimed chitin production, they used a 100-year-old chemical and energy-intensive process that degraded chitin by reducing its molecular weight. This process also results in a large degree of deacetylation of chitin, producing chitosan, a polymer with different properties. Unfortunately, the lack of rigor in terminology has led to confusion in the markets about the actual properties of chitin as a material versus chitosan.

In 2018, there were only two functioning facilities identified: Tidal Vision, Inc. [36] and CarboMer, Inc. [37]. Tidal Vision is a company that manufactures chitin-based and chitosan-based products and serves various industries including textile, cosmetic, water treatment, agriculture, food, pharmaceutical, and so forth, and also sells raw material to research institutions and laboratories [36]. The company claims to use a “patent-pending, closed-loop processing system” to extract chitin from crab shells, although the company does not provide the technology of chitin isolation. CarboMer, Inc. [37] is the second company that appears in numerous market reports as a producer of chitin; however, we were unable to find either chitin or its derivative, chitosan, in the company’s product list. The company sells polyamino acids, polyglycolides and polylactides, collagens, poly(3-hydroxybutyrate), PLA, poly(estradiol phosphate), poly(ethylene adipate), poly(glycolic acid), and polyinosinic-polycytidylic acids as biopolymers [37].

Chitin is used in animal feed as a dietary supplement. It is reported to promote animal growth, to improve adsorption of nutrients, and to inhibit the effect of harmful microorganisms [38]. Its properties also make the polymer an ideal material for the following uses in agriculture: (1) as a fertilizer, (2) as a fungicide and pesticide in

crop protection, (3) as an agent to improve seed quality (as well as crop yield and quality), and (4) as a plant growth stimulator; it also acts as amplifier of the beneficial chitinolytic microbes [39]. Chitin is used in environmental applications as an effective biosorbent, due to presence of both hydroxyl- and acetamide-moieties (easily modifiable into amine functionality), which demonstrate high adsorption potential for the removal of various metal ions from water sources [40]. Chitin, in the form of whiskers or nanofibers, can be utilized during manufacturing processes as an additive to reinforce existing materials (packaging, fibers, etc.) [41].

Key market players, however, are approaching the market with advanced high-quality *medical* products of higher efficacy. Unitika, Ltd. (Japan) [42] marketed a chitin-containing non-woven dressing (Beschitin W) for the treatment of burns and demonstrated its superior performance in speed of healing, wound adherence, exudate absorption, and scar minimization. In 1970, multiple new companies appeared on the market. Eisai Co., Ltd. produces wound dressings from chitin, Chitipack S[®] and Chitipack P[®] [43], which are used in the treatment of traumatic wounds preventing the formation of scar tissue [44]. Syvek-Patch[®] produced by Marine Polymer Technologies, Inc. is made of microfiber chitin [45], as is Excel Arrest[®] dressing from Hemostasis, LLC [46]. Numerous opportunities for chitin products can be found in selected reviews [20–25].

4.2.3 *Current Chitin Isolation Methods*

Chitin isolation targets a biomass source generated by U.S.-based fisheries as a costly waste that can be turned into valuable products. Yet, currently, chitin is isolated from crustacean biomass via a pulping process. Pulping typically includes three steps: (1) demineralization to remove calcium carbonate present in a shell matrix (using acids (e.g., HCl)), (2) deproteinization to remove proteins (conducted using hydroxides (e.g., NaOH)), and (3) bleaching/discoloration (using organic solvents [47] or oxidation agents [48]). Because pulping is conducted at relatively high temperatures (70–100 °C) and usually for a prolonged time [49, 50], the process adequately removes both proteins and shell inorganics but generates a large amount of waste.

Manufacturing 1 kg of chitin using the pulping method requires 10 kg of biomass, 300 L of freshwater, 9 kg of HCl, 8 kg of NaOH, and 1.2 kWh of electricity. The liquid waste generated is equal to the input freshwater volume plus the process water; the overall amount of waste per 1 kg of chitin exceeds 500 L [26]. In addition, the emission of CO₂ is estimated to be 0.9 kg/kg of chitin [26]. Such high cost involved in the production of chitin and the huge quantity of generated waste resulted in the pulping process raising public and governmental concerns. As a result, there is no chitin producing plant that uses acid/base treatment in the United States [51]. In addition, crustacean shells contain a host of potentially valuable components in addition to chitin, including other biopolymers, such as proteins, small molecules, such as astaxanthin that have medical value, and minerals, such as calcite that may

be useful as construction materials; all of them get destroyed during the pulping process.

Lastly, harsh conditions used in isolation were found to decrease the quality of the isolated chitin, to promote deacetylation and depolymerization, and to result in a lack of reproducible high-quality polymer product [52]. However, many applications require specific polymer properties, and the strength of materials has been proven to be governed by the molecular weight and the degree of acetylation. We have shown (and will detail it below in this chapter) that high-molecular weight chitin is critical for the preparation of materials with different shapes (fibers, films, packages, hydrogels, beads, and electrospun mats). This host of new materials and the preparation of chitin composites and blends [53–68] are made possible by an ionic liquid [69] solution-based process.

4.3 Startup to Scale-up

4.3.1 *The Beginning: Business Opportunity*

In 2010, Rogers demonstrated the dissolution and extraction of the biopolymer chitin directly from shrimp shells [70]. Before that, no one had reported the direct dissolution of crustacean biomass or the extraction of chitin polymer from it using ionic liquids. The IL 1-ethyl-3-methylimidazolium acetate ($[C_2C_1im][OAc]$) was shown to be an excellent solvent for chitin [71]. Using this IL, microwave irradiation facilitated the dissolution and demineralization of crustacean biomass and resulted in the extraction of all available chitin in minutes. The polymer maintained its high-molecular weight resulting in a material with high strength and unprecedented high quality. At that point, this extraction method was demonstrated on a 100 mL scale using a domestic microwave.

The quantities of isolated polymers are critical to many materials applications and must be produced at a larger scale. For instance, co-dissolved with alginic acid, high-molecular weight chitin–IL solutions were shown to be suitable for the preparation of spun chitin–calcium alginate fibers [63, 70, 72], for intracutaneous biocompatibility testing, and wound-healing studies. Using a domestic microwave and a lab-scale fiber pulling setup, it took 3 weeks to prepare only 6 g of bandages [63]. Using a somewhat larger setup, with a small manufacturing, custom-made fiber extruder, required a minimum loading of 1 kg of the solution to produce 1,000 m of monofilament fiber. Clearly, a prototype was necessary to make scaled-up quantities for the preparation of sustainable, high-value chitin materials.

4.3.2 *Baby Steps: Laboratory Demonstration Pilot Unit (Alabama Innovation Grant)*

Seeking funding to scale up chitin production, we turned our attention to the Alabama Department of Commerce's "Accelerate Alabama" Program, particularly to the Alabama Innovation Fund (AIF) that was established "to maximize the use of the State's economic development resources by leveraging annual research and development expenditures by public institutions and generate high technology resources which can be used to support economic development activities" [73].

The AIF Fund mainly supported research collaborations among universities and industries working on research that could be economically beneficial to the state. If chitin extraction at scale was successful, there would be new and better business options for the seafood industries by utilizing shrimp shells, an industrial waste product. A collaboration was established with the Gulf Coast Agricultural and Seafood Cooperative [74] in Bayou La Batre, AL. They had built a seafood waste drying/pulverizing facility with the support of the Alabama Farmers Market Authority. The facility collects crustacean biomass waste from resident fishermen and biomass-handling plants that are then pressed for protein removal, passed through a fluidized bed dryer for dewatering, and shredded before bagging. At maximum capacity, the plant can process up to 10 tons of shrimp shells a day into sterilized, dry chitin-containing material. Finding uses for this waste material could save the seafood industry of Alabama hundreds of thousands of dollars a month in waste disposal costs as well as opportunities for new jobs as the shrimp shells can be converted into value-added products.

In 2012, an Alabama Innovation Fund (AIF) grant was given to The University of Alabama researchers and startup company 525 Solutions, Inc. to build a Laboratory Demonstration Pilot Unit (LDPU) that would enable scaling up the process of extracting chitin from the bench scale to a prototype scale needed for the manufacture of chitin-based products. The Department of Commerce award was part of a more complex project that included research and development, a business plan and market development, product demonstration, and prototype construction. The project was divided into several major phases: (1) design and development of a continuous process for chitin extraction, (2) scale-up of the process, (3) construction of a LDPU, (4) R&D of new chitin-based materials and new product-development technologies, and (5) demonstration of new products to provide higher value to the seafood wastes.

Under this Alabama Department of Commerce award, Rogers' group developed a prototype capable of the continuous processing of shellfish waste. The LDPU (Fig. 4.2) included a closed-loop where biomass and ionic liquid could be cycled through until the dissolution was complete. This provided excellent control over the heating rates of the solution. The unit consisted of a 3 L, glass-jacketed reactor (Fig. 4.2a) with an overhead mechanical stirrer (Fig. 4.2b) attached to a continuous-flow 2 kW microwave (Industrial Microwave Systems, Fig. 4.2c). The pumping was conducted using a peristaltic pump (Cole-Parmer, Fig. 4.2d).

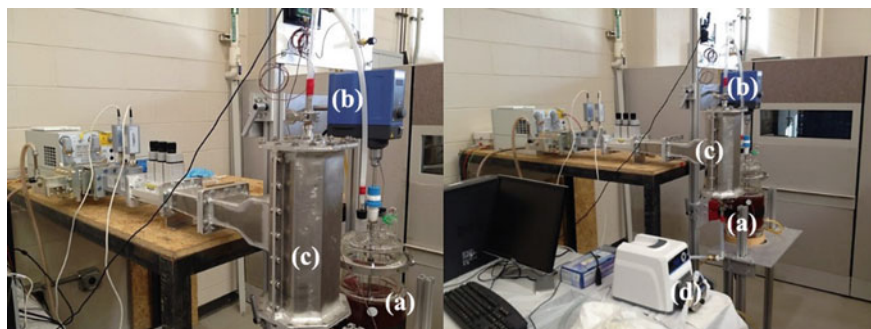


Fig. 4.2 LDPU consisted of a 3 L glass-jacketed reactor (a), overhead mechanical stirrer (b), continuous-flow 2 kW microwave (c), and a peristaltic pump (d)

After an optimization study, continuous chitin dissolution was conducted using 3 L of $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ under cylindrical, 2 kW continuous microwave heating. The IL was fed into the unit and heated to 95–98 °C. Only 10% of the microwave capacity was necessary to achieve the dissolution of the biomass and not decompose the IL. The run suggested that the IL effectively absorbs the microwave energy and can be treated continuously in a microwave. To ensure that the recycled IL could be reclaimed and reused with no significant loss, the IL was circulated through the microwave for several cycles, and no obvious degradation was observed. This scaled dissolution of chitin in IL by microwave heating provided essential knowledge (thermal exchange data, microwave energy input/output, microwave energy efficiency, and cooling rate) for scaling up to a *pilot* system.

In addition, as a part of the project to provide higher value to the seafood wastes, we also focused on R&D of new chitin-based materials and new product development technologies. Chitin–IL solutions were shown to be suitable for the preparation of spun fibers, films, hydrogels, beads, and electrospun mats providing a route to a host of new materials (Fig. 4.3): chitin fibers (wet: a, dry: b), chitin electrospun nanomat (c, d), chitin beads (e, f), chitin hydrogel (g, h), and chitin film (i, j). [54–68].

4.3.3 Bench to Pilot Scale Prototype: Leveraging Sorbent Production Technology

Using AIF funds, dissolution of chitin in an ionic liquid by microwave heating using LDPU provided essential knowledge and revealed useful data needed for the further scale-up to a 20 L *pilot* system. Based on our earlier results with cellulose [75], we planned to develop and optimize the pilot scale-up process for this technology. However, from our earlier studies with cellulose we learned that there were few examples of successful academia-to-industry technology transfers. Successful transfer would require ensuring that both the technology and processes were scalable and, more

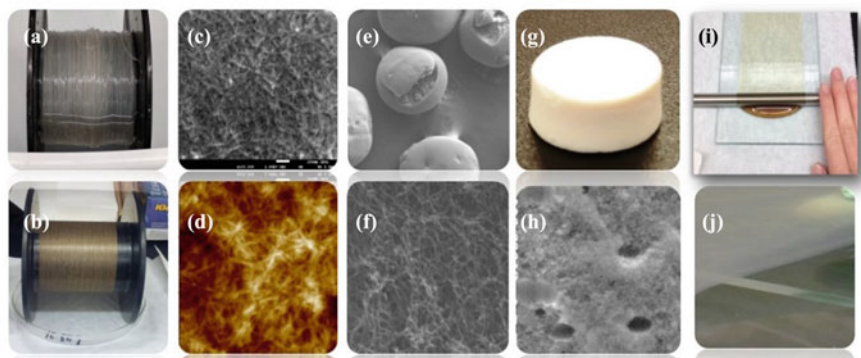


Fig. 4.3 Chitin products: chitin fibers (wet: **a**, dry: **b**), chitin electrospun nanomat (SEM: **c**, AFM: **d**), chitin beads (**e**), and chitin bead interior (**f**), chitin hydrogel (**g**) and hydrogel interior (**h**), wet chitin film cast on a glass plate (**i**) and wet chitin film in water (**j**). Images support the work described in our publications [54–68]

importantly, that the development of high-value end products was possible with a successful business plan rather than a scale-up with no purpose.

Considering that the extraction process could be key to a “chitin economy” and would, upon its success, provide a revenue stream for shrimpers to utilize their waste while helping to develop sustainable/green products, we started looking into ways to leverage our chitin extraction technology. Our attention turned to a U.S. Department of Energy (DOE) Nuclear Energy Program (uranium recovery from seawater), a part of U.S. DOE efforts that included collaborative efforts of several universities and small businesses.

The University of Alabama researchers and startup company 525 Solutions, Inc. combined efforts to develop highly economical and biodegradable uranium-selective sorbents, specifically for the U.S. DOE Nuclear Energy Program aimed at the extraction of uranium from seawater. The concept of sorbents was based on our previous work, where we investigated the electrospinnability of IL-extracted chitin solutions from $[C_2C_1im][OAc]$ [76]. The project focused on the delivery of the product to government-designated mining companies and at the same time proposed leveraging the U.S. DOE resources to generate a sustainable chitin products business. Such leveraging would allow both economic development and creation of jobs in R&D of chitin products and fishing industries. This way, the chitin nanomaterials would serve as a platform for the delivery of chitin to U.S. markets, as well as providing a range of medium- to high-value applications in medicine, energy, and environmental restoration sectors.

Because there was no existing industrial base for the extraction of uranium from seawater, the entry decision thus revolved more around how to build a successful business for this opportunity. If the commercialization strategy was built only around the sale of the sorbent, the company would cease to exist if government support of the program ended before an industry emerged. However, as mentioned earlier in

this chapter, *numerous* market opportunities were emerging based on the underlying technology, chitin extraction. The ability to produce not only products from chitin, but chitin itself, provided a competitive advantage to diversify the range of products and enter several profitable specialized markets, while at the same time developing the sorbents for the DOE Nuclear Energy Program. Such leveraging would lower the bulk cost of the sorbent by building high-end markets that would help pay for the process development and economy of scale.

For 2014–2015, a \$1.5 million grant was funded by the U.S. DOE Small Business Innovation Research Program, “Bench to pilot scale prototype for electrospinning biorenewable chitin sorbents for uranium from seawater: Process development, cost, and environmental analysis” (*DOE-SBIR Grant No. DE-SC0010152, Phase I/II*). The ultimate goal of this project was to collect the industrial process parameters, to conduct reliable economic estimates, and ultimately to generate data for the full-scale operating plant design.

To address the scalability of the IL technology platform for biomass processing, Rogers’ group (together with 525 Solutions, Inc.) refined the pilot plant operating conditions and plant design and prepared input-output diagrams of the process. This provided the relationships between the major equipment of a pilot plant facility and the piping of the process flow together with all required equipment and instrumentation. Next, a scaled, highly automated customized 20-L early pilot stage system amenable for chitin extraction was built. It contained a custom-design, continuous-flow stirred-tank reactor (CSTR) and a 2 kW microwave (Fig. 4.4).

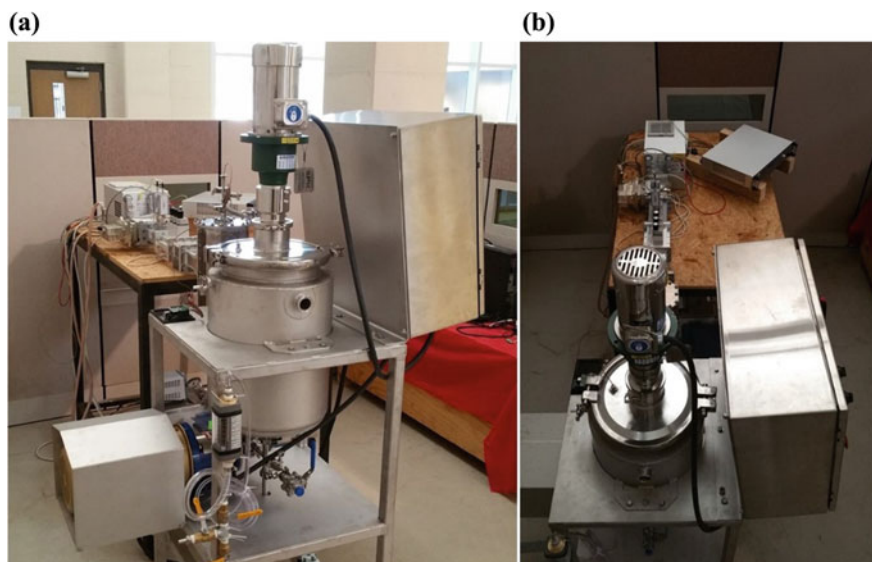


Fig. 4.4 A continuous scaled, automated, and customized 20-L early pilot stage system amenable for chitin extraction. (a): side view, (b): top view

After multiple, unsuccessful pilot trials, the optimal conditions (biomass load, temperature, flow rate through the microwave, residual time in the microwave, and process time) for the dissolution of biomass in the reactor were determined. Optimal conditions resulted in a high yield of approximately 95% (as percent of available chitin in biomass). A mass balance was completed using the optimal conditions of biomass dissolution based on different reagent streams, reagent consumption, and product recovery (i.e., using multi-parametric input). This permitted multi-step evaluations for the determination of the process inputs and outputs based on production cycles.

An energy balance was completed using the overall energy consumption in each energy-demanding step based on production. Cost analyses were conducted where scale-up of some 30 equipment items was handled either through increasing the size or capacity of the equipment (so-called economies of scale) or by increasing throughput by projecting the purchase of additional units of defined capacity. To date, no other entity has scaled this IL process to this size.

This project resulted in a fully engineered system, developed key engineering data and diagrams, as well as determined the equipment needed in a full-scale operating plant. Processing performance testing was conducted while manufacturing chitin on a pilot scale. The results of these studies were used to establish manufacturing capability and process robustness and to mitigate the risks before committing to a full-scale production process.

4.3.4 Mari Signum, Mid-Atlantic: The First Facility to Use Ionic Liquid-Based Chitin Extraction at a Production Scale

The knowledge obtained in these efforts was used to raise capital investment for building and operating a biomass/IL facility. Mari Signum, Mid-Atlantic, LLC (Mari Signum) [77] was formed as a chitin and chitin materials production company. The ultimate goal of Mari Signum, Mid-Atlantic, LLC is to become a sustainable source of high-quality chitin as well as chitin-based products developed in-house.

Mari Signum acquired the worldwide exclusive license for the portfolio of intellectual property (IP) that protects the manufacture of chitin. This IP will allow Mari Signum to maintain its position in the market and protect its competitive advantages. The licensing granted Mari Signum not only the rights to the chitin-extraction patents, but also all patents associated with high-value products. These products from chitin, and not chitin itself, would, indeed, be key components in the development of a “chitin economy”.

Mari Signum’s facility will be the first of its kind to use IL-based processing on a manufacturing scale that will allow the generation of sufficient supplies of high-quality chitin, which is unobtainable by any known chemical pulping processes. Mari Signum is currently building a processing plant for chitin isolation from crustacean

biomass. The ability of Mari Signum to produce not only chitin itself but also products from chitin will give Mari Signum a competitive advantage to diversify the range of its products and to enter several profitable specialized markets.

4.4 Conclusion and Outcome

Chitin represents a billion-dollar industry worldwide, but despite the promising properties of chitin (and the large amounts of available shellfish waste in the United States), its potential production at an industrial level has been scarcely explored. There is no chitin producing plant in the United States mainly because of the current environmentally unfriendly chitin isolation process. At the same time, chitin isolation extends far beyond producing chitin itself. There are many opportunities for the manufacture of novel chitin products from shrimp shell waste that have not yet been tapped. Such high-value products will cause high industrial growth and have a positive environmental impact. A large enough chitin supply will be needed for the chitin industry to become a game-changer in a sustainable society.

Even with a billion-dollar industry opportunity, our own experience demonstrates that the transition of technology from academia to industry is rarely a straightforward process. As the technology progressed, it required proceeding through several time- and effort-consuming stages with each one successively larger in scale—(bench, pilot, demonstration, and production scale). Each stage used the knowledge accumulated from the previous round of scale-up. With the benefit of hindsight, this story might be useful for others who are ready to take this journey.

Hopefully, chitin products will make existing plastics obsolete.

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References

1. Plastics market analysis by product (PE, PP, PVC, PET, polystyrene, engineering thermoplastics), by application (film & sheet, injection molding, textiles, packaging, transportation, construction) and segment forecasts to 2020. Grand View Research, Inc., 2015. Available at: <http://www.grandviewresearch.com/industry-analysis/global-plastics-market>. Last accessed 04-02-18
2. University of Georgia (2017) More than 8.3 billion tons of plastics made: most has now been discarded. Science Daily, 19 July 2017. Available at: <https://www.sciencedaily.com/releases/2017/07/170719140939.htm>. Last accessed 12-10-19

3. Geyer R, Jambeck JR, Law KL (2017) Production, use, and fate of all plastics ever made. *Sci Adv* 3:e1700782. <https://doi.org/10.1126/sciadv.1700782>
4. Ellen MacArthur Foundation 2016 Report. Rethinking the future of plastics: <https://www.ellenmacarthurfoundation.org/our-work/activities/new-plastics-economy/2016-report>. Last accessed 07-28-19
5. Tunnicliffe H (2017) Turning ocean trash into cash. *TCE: the chemical engineer* 913/914:36–38. Available at: <https://www.thechemicalengineer.com/features/turning-ocean-trash-into-cash/> Last accessed 07-16-19
6. North EJ, Halden RU (2013) Plastics and environmental health: the road ahead. *Rev Environ Health* 28:1–8. <https://doi.org/10.1515/reveh-2012-0030>
7. Popa V (2018) Biomass for fuels and biomaterials. In: Popa VI, Volf I (eds) *Biomass as renewable raw material to obtain bioproducts of high-tech value*, Elsevier, pp 1–37. <https://doi.org/10.1016/B978-0-444-63774-1.00001-6>
8. Intro to plantbottle packaging. Available at: <https://www.coca-colacompany.com/plantbottle-technology>. Last accessed 04-19-18
9. Edge M, Hayes M, Mohammadian M, Allen NS, Jewitt TS, Brems K, Jones K (1991) Aspects of poly(ethylene terephthalate) degradation for archival life and environmental degradation. *Polym Degrad Stab* 32:131–153. [https://doi.org/10.1016/0141-3910\(91\)90047-U](https://doi.org/10.1016/0141-3910(91)90047-U)
10. Allen NS, Edge M, Mohammadian M, Jones K (1994) Physicochemical aspects of the environmental degradation of poly(ethylene terephthalate). *Polym Degrad Stab* 43:229–237. [https://doi.org/10.1016/0141-3910\(94\)90074-4](https://doi.org/10.1016/0141-3910(94)90074-4)
11. Rogers RD (2015) Eliminating the need for chemistry. *C&EN* 93(48):42–43. <https://cen.acs.org/articles/93/i48/Eliminating-Need-Chemistry.html>
12. Gao X, Chen X, Zhang J, Guo W, Jin F, Yan N (2016) Transformation of chitin and waste shrimp shells into acetic acid and pyrrole. *ACS Sustain Chem Eng* 4:3912–3920. <https://doi.org/10.1021/acssuschemeng.6b00767>
13. Prudden JF, Migel P, Hanson P, Friedrich L, Balassa L (1970) The discovery of a potent pure chemical wound-healing accelerator. *Am J Surg* 119:560–564. [https://doi.org/10.1016/0002-9610\(70\)90175-3](https://doi.org/10.1016/0002-9610(70)90175-3)
14. Jayakumar R, Prabakaran M, Kumar PTS, Sudheesh Kumar PT, Nair SV, Furnike T, Tamura H (2011) Novel chitin and chitosan materials in wound dressing. In: Laskovski AN (ed) *Biomedical engineering trends in materials science*, InTech 3–24. <https://doi.org/10.5772/13509>
15. Vázquez JA, Rodríguez-Amado I, Montemayor MI, Fraguas J, González M del P, Murado MA (2013) Chondroitin sulfate, hyaluronic acid and chitin/chitosan production using marine waste sources: characteristics, applications and eco-friendly processes: a review. *Mar Drugs* 11:747–774. <https://doi.org/10.3390/md11030747>
16. Mori T, Okumura M, Matsuura M, Ueno K, Tokura S, Okamoto Y, Minami S, Fujinaga T (1997) Effects of chitin and its derivatives on the proliferation and cytokine production of fibroblasts *in vitro*. *Biomaterials* 18:947–951. [https://doi.org/10.1016/S0142-9612\(97\)00017-3](https://doi.org/10.1016/S0142-9612(97)00017-3)
17. Hirano S, Nakahira T, Nakagawa M, Kim SK (1999) The preparation and application of functional fibres from crab shell chitin. *J Biotechnol* 70:373–377. [https://doi.org/10.1016/S0079-6352\(99\)80130-1](https://doi.org/10.1016/S0079-6352(99)80130-1)
18. Wan ACA, Tai BCU (2013) Chitin—a promising biomaterial for tissue engineering and stem cell technologies. *Biotech Adv* 31:1776–1785. <https://doi.org/10.1016/j.biotechadv.2013.09.007>
19. Barber PS, Kelley SP, Griggs CS, Wallace S, Rogers RD (2014) Surface modification of ionic liquid-spun chitin fibers for the extraction of uranium from seawater: seeking the strength of chitin and the chemical functionality of chitosan. *Green Chem* 16:1828–1836. <https://doi.org/10.1039/C4GC00092G>
20. Muzarelli RAA, Boudrant J, Meyer D, Manno N, DeMarchis M, Paoletti MG (2012) Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: a tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. *Carbohydr Polym* 87:995–1012. <https://doi.org/10.1016/j.carbpol.2011.09.063>

21. Dutta PK, Dutta J, Tripathi VS (2004) Chitin and chitosan: chemistry, properties and applications. *J Sci Ind Res* 63:20–31.
22. Domard A (2011) A perspective on 30 years research on chitin and chitosan. *Carbohydr Polym* 84:696–703. <https://doi.org/10.1016/j.carbpol.2010.04.083>
23. Tharanathan RN, Kittur FS (2003) Chitin—the undisputed biomolecule of great potential. *Critical Rev Food Sci Nutr* 43:61–87. <https://doi.org/10.1080/10408690390826455>
24. Synowiecki J, Al-Khateeb NA (2003) Production, properties, and some new applications of chitin and its derivatives. *Critical Rev Food Sci Nutr* 2:145–171. <https://doi.org/10.1080/10408690390826473>
25. Ravi Kumar MNV (2000) A review of chitin and chitosan applications. *React Funct Polym* 46:1–27. [https://doi.org/10.1016/S1381-5148\(00\)00038-9](https://doi.org/10.1016/S1381-5148(00)00038-9)
26. Chitin market: agrochemical end use industry segment inclined towards high growth—moderate value during the forecast period: global industry analysis (2012–2016) and opportunity assessment (2017–2027). <https://www.futuremarketinsights.com/reports/chitin-market>. Last accessed 04-02-18
27. Yang T-L (2011) Chitin-based materials in tissue engineering: applications in soft tissue and epithelial organ. *Int J Mol Sci* 12:1936–1963. <https://doi.org/10.3390/ijms12031936>
28. Khor E, Lim LY (2003) Implantable applications of chitin and chitosan. *Biomaterials* 24:2339–2349. [https://doi.org/10.1016/S0142-9612\(03\)00026-7](https://doi.org/10.1016/S0142-9612(03)00026-7)
29. Mi F-L, Shyu S-S, Lin Y-M, Wu Y-B, Peng C-K, Tsai Y-H (2003) Chitin/PLGA blend microspheres as a biodegradable drug delivery system: a new delivery system for protein. *Biomaterials* 24:5023–5036. [https://doi.org/10.1016/S0142-9612\(03\)00413-7](https://doi.org/10.1016/S0142-9612(03)00413-7)
30. Rejinold NS, Chennazhi KP, Tamura H, Nair SV, Jayakumar R (2011) Multifunctional chitin nanogels for simultaneous drug delivery, bioimaging, and biosensing. *ACS Appl Mater Interfaces* 3:3654–3665; 11.13832. <https://doi.org/10.1021/am200844m>
31. Ding F, Deng H, Du Y, Shi X, Wang Q (2014) Emerging chitin and chitosan nanofibrous materials for biomedical applications. *Nanoscale* 6(16):9477–9493. <https://doi.org/10.1039/C4NR02814G>
32. Singh R, Shitiz K, Singh A (2017) Chitin and chitosan: biopolymers for wound management. *Int Wound J* 14:1276–1289. <https://doi.org/10.1111/iwj.12797>
33. Jayakumar R, Prabaharan M, Sudheesh Kumar PT, Nair SV, Tamura H (2011) Biomaterials based on chitin and chitosan in wound dressing applications. *Biotech Adv* 29:322–337. <https://doi.org/10.1016/j.biotechadv.2011.01.005>
34. Shigemasa Y, Minami S (1996) Applications of chitin and chitosan for biomaterials. *Biotech Genetic Eng Rev* 13:383–420. <https://doi.org/10.1080/02648725.1996.10647935>
35. Trutnau M, Bley T, Ondruschka J (2011) Chapter 1: Chitosan from fungi. In: Davis SP (ed) *Chitosan: manufacture, properties, and usage*, Nova Science Publishers, Inc., New York, NY, pp. 1–70.
36. Tidal Vision, USA. <https://tidalvisionusa.com/chitosan/>. Last accessed 04-03-18
37. CarboMer. <https://www.carbomer.com/biopolymers>. Last accessed 04-03-18
38. Shiau S-Y, Yu Y-P (1998) Chitin but not chitosan supplementation enhances growth of grass shrimp, *Penaes monodon*. *J Nutr* 128:908–912. <https://doi.org/10.1093/jn/128.5.908>
39. Sharp RG (2013) A review of the applications of chitin and its derivatives in agriculture to modify plant-microbial interactions and improve crop yields. *Agronomy* 3:757–793. <https://doi.org/10.3390/agronomy3040757>
40. Bhatnagar A, Sillanpää M (2009) Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater—a short review. *Adv Colloid Interface Sci* 152:26–38. <https://doi.org/10.1016/j.cis.2009.09.003>
41. Araki J, Yamanaka Y, Ohkawa K (2012) Chitin-chitosan nanocomposite gels: reinforcement of chitosan hydrogels with rod-like chitin nanowhiskers. *Polymer J* 44:713–717. <https://doi.org/10.1038/pj.2012.11>
42. Unitika history creates its next history. <https://www.unitika.co.jp/e/company/history/>. Last accessed 04-04-18
43. Eisai Co. <https://www.eisai.com/index.html>, last accessed 04-04-18

44. Minami S, Okamoto Y, Miyatake A, Matsushashi A, Kitamura Y, Tanigawa T, Tanaka Y, Shigemasa Y (1996) Chitin induces type IV collagen and elastic fiber in implanted non-woven fabric of polyester. *Carbohydrate Polym* 29:295–299. [https://doi.org/10.1016/S0144-8617\(96\)00078-1](https://doi.org/10.1016/S0144-8617(96)00078-1)
45. SyvekExcel. <http://syvek.com/>. Last accessed 04-04-18
46. Technical Information: ExcelArrest[®] XT. <http://www.hemostasisllc.com/excelarrest-technfo.html>. Last accessed 04-04-18
47. Poeloengasih CD, Hernawan, Angwar M (2008) Isolation and characterization of chitin and chitosan prepared under various processing times. *Indo J Chem* 8:189–192. <https://doi.org/10.22146/ijc.21635>
48. Beaney P, Lizardi-Mendoza J, Healy M (2005) Comparison of chitins produced by chemical and bioprocessing methods. *J Chem Tech Biotech* 80:145–150. <https://doi.org/10.1002/jctb.1164>
49. Rinaudo M (2006) Chitin and chitosan: properties and applications. *Prog Polym Sci* 31:603–632. <https://doi.org/10.1016/j.progpolymsci.2006.06.001>
50. Khoushab F, Yamabhai M (2010) Chitin research revisited. *Mar Drugs* 8:1988–2012. <https://doi.org/10.3390/md8071988>
51. Shamshina JL, Barber PS, Gurau G, Griggs CS, Rogers RD (2017) Pulping of crustacean waste using ionic liquids: to extract or not to extract. *ACS Sust Chem Eng* 4:6072–6081. <https://doi.org/10.1021/acssuschemeng.6b01434>
52. Younes I, Rinaudo M (2015) Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Mar Drugs* 13:1133–1174. <https://doi.org/10.3390/md13031133>
53. Silva SS, Mano JF, Reis RL (2017) Ionic liquids in the processing and chemical modification of chitin and chitosan for biomedical applications. *Green Chem* 19:1208–1220. <https://doi.org/10.1039/C6GC02827F>
54. King C, Shamshina JL, Gurau G, Berton P, Khan NFAF, Rogers RD (2017) A platform for more sustainable chitin films from an ionic liquid process. *Green Chem* 19:117–126. <https://doi.org/10.1039/C6GC02201D>
55. Shen X, Shamshina JL, Berton P, Bandomir J, Wang H, Gurau G, Rogers RD (2016) Comparison of hydrogels prepared with ionic-liquid-isolated vs commercial chitin and cellulose. *ACS Sustainable Chem Eng* 4:471–480. <https://doi.org/10.1021/acssuschemeng.5b01400>
56. Kadokawa J (2016) Dissolution, gelation, functionalization, and material preparation of chitin using ionic liquids. *Pure Appl Chem* 88:621–629. <https://doi.org/10.1515/pac-2016-0503>
57. Shamshina JL, Zavgorodnya O, Bonner JR, Gurau G, Di Nardo T, Rogers RD (2017) “Practical” electrospinning of biopolymers in ionic liquids. *ChemSusChem* 10:106–111. <https://doi.org/10.1002/cssc.201601372>
58. Zavgorodnya O, Shamshina JL, Bonner JR, Rogers RD (2017) Electrospinning biopolymers from ionic liquids requires control of different solution properties than volatile organic solvents. *ACS Sustain Chem Eng* 5:5512–5519. <https://doi.org/10.1021/acssuschemeng.7b00863>
59. Turner MB, Spear SK, Holbrey JD, Rogers RD (2004) Production of bioactive cellulose films reconstituted from ionic liquids. *Biomacromol* 5:1379–1384. <https://doi.org/10.1021/bm049748q>
60. Turner MB, Spear SK, Holbrey JD, Daly DT, Rogers RD (2005) Ionic liquid-reconstituted cellulose composites as solid support matrices for biocatalyst immobilization. *Biomacromol* 6:2497–2502. <https://doi.org/10.1021/bm050199d>
61. Sun N, Swatloski RP, Maxim ML, Rahman M, Harland AG, Haque A, Spear SK, Daly DT, Rogers RD (2008) Magnetite-embedded cellulose fibers prepared from ionic liquid. *J Mater Chem* 18:283–290. <https://doi.org/10.1039/B713194A>
62. Bagheri M, Rodríguez H, Swatloski RP, Spear SK, Daly DT, Rogers RD (2008) Ionic liquid-based preparation of cellulose–dendrimer films as solid supports for enzyme immobilization. *Biomacromol* 9:381–387. <https://doi.org/10.1021/bm701023w>
63. Shamshina JL, Gurau G, Block LE, Hansen LK, Dingee C, Walters A, Rogers RD (2014) Chitin–calcium alginate composite fibers for wound care dressings spun from ionic liquid solution. *J Mater Chem B* 2:3924–3936. <https://doi.org/10.1039/C4TB00329B>

64. Maxim ML, White JF, Block LE, Gurau G, Rogers RD (2012) Advanced biopolymer composite materials from ionic liquid solutions in ionic liquids: science and applications. In: Visser AE, Bridges NJ, Rogers RD (eds) *Ionic liquids: science and applications*, ACS Symp Ser 1117:167–187. <https://pubs.acs.org/doi/10.1021/bk-2012-1117.ch007>
65. Takegawa A, Murakami M, Kaneko Y, Kadokawa J (2010) Preparation of chitin/cellulose composite gels and films with ionic liquids. *Carbohydr Polym* 79:85–90. <https://doi.org/10.1016/j.carbpol.2009.07.030>
66. Singh N, Koziol KKK, Chen J, Patil AJ, Gilman JW, Trulove PC, Kafienah W, Rahatekar SS (2013) Ionic liquids-based processing of electrically conducting chitin nanocomposite scaffolds for stem cell growth. *Green Chem* 15:1192–1202. <https://doi.org/10.1039/C3GC37087A>
67. Mundsinger K, Müller A, Beyer R, Hermanutz F, Buchmeiser MR (2015) Multifilament cellulose/chitin blend yarn spun from ionic liquids. *Carbohydr Polym* 131:34–40. <https://doi.org/10.1016/j.carbpol.2015.05.065>
68. Sun N, Li W, Stoner B, Jiang X, Lu X, Rogers RD (2011) Composite fibers spun directly from solutions of raw lignocellulosic biomass dissolved in ionic liquids. *Green Chem* 13:1158–1161. <https://doi.org/10.1039/C1GC15033B>
69. Shamshina JL, Berton P, Rogers RD (2019) Advances in functional chitin materials: a review. *ACS Sustain Chem Eng* 7:6444–6457. <https://doi.org/10.1021/acssuschemeng.8b06372>
70. Qin Y, Lu X, Sun N, Rogers RD (2010) Dissolution or extraction of crustacean shells using ionic liquids to obtain high molecular weight purified chitin and direct production of chitin films and fibers. *Green Chem* 12:968–971. <https://doi.org/10.1039/C003583A>
71. Wang H, Gurau G, Rogers RD (2014) Dissolution of biomass using ionic liquids. In: Zhang S, Wang J, Lu X, Zhou Q (eds) *Structures and interactions of ionic liquids* 151. Springer, Berlin, Heidelberg, pp 79–105. https://doi.org/10.1007/978-3-642-38619-0_3
72. Shamshina JL, Zavgorodnya O, Rogers RD (2018) Advances in processing chitin as promising biomaterial from ionic liquids. In: Itoh T, Koo Y-M (eds) *Application of ionic liquids in biotechnology*. Advances in biochemical engineering/biotechnology. Springer, Cham, pp. 177–198. https://doi.org/10.1007/10_2018_63
73. Alabama Innovation Fund (AIF): Alabama EPSCOR. <https://alepscor.org/alabama-innovation-fund/>. Last accessed 4-03-18
74. Gulf Coast Agricultural and Seafood COOP. <https://www.amcref.com/impact/gulf-coast-agriculture-and-seafood-co-op/>. Last accessed 07-28-19
75. Zavgorodnya O, Shamshina JL, Berton P, Rogers RD (2017) Translational research from academia to industry: following the pathway of George Washington Carver. In: Shiflett MB, Scurto AM (eds) *Ionic liquids: current state and future directions*, ACS Symp Ser 1250:17–33. <https://doi.org/10.1021/bk-2017-1250.ch002>
76. Barber PS, Griggs CS, Bonner JR, Rogers RD (2013) Electrospinning of chitin nanofibers directly from an ionic liquid extract of shrimp shells. *Green Chem* 15:601–607. <https://doi.org/10.1039/C2GC36582K>
77. Mari Signum, Mid-Atlantic. <http://www.marisignum.com/>. Last Accessed 04-19-18